Proceedings of the Environmental Protection Agency PUBLIC MEETING ON WASTE LEACHING Session II - Modeling and Risk Assessment

Importance of Leachate Tests in the Assessment Process - Dr. Ishwar Murarka

Dr. Ishwar Murarka, of ISH Inc., provided an overview of how leachate test results are used in modeling and risk assessment. A copy of Dr. Murarka's presentation materials is available through the following link: murarka2.pdf. He enumerated the general types of leaching tests:

- Batch Equilibrium a single test, this is the approach used by the TCLP
- Column tests usually a single test, this approach is laboratory-based, and may comprise either complete or partial renewal of the leachant, or no renewal at all
- Partitioning/Distribution Coefficient-based not a test at all, but a calculation for organic materials based on partitioning coefficients or distribution coefficients between dissimilar liquid phases.
- Solubility-based not a test at all, but for many metals, there are data available in the literature that describe the activity (concentration) of a given mineral form of the metal at a given pH. Having these data, the concentration in the leachate is simply calculated.
- Field pore water composition this approach does not really constitute a leaching test. You simply sample and analyze the *in situ* pore water.

Leaching tests serve to quantify the source terms for fate and transport modeling. The purpose of the leaching tests is to obtain aqueous phase concentration(s) of constituent(s) which are released from solids when placed in a land disposal unit(s). The underlying assumption is, if the constituent doesn't leach from the waste, then land disposal of that constituent is not a threat to groundwater. The leachate concentration(s) constitute the source term for the transport and fate modeling which is coupled with the effects information to estimate potential risk. This presents one of the problems with the TCLP - the test does not provide a source term for modeling long-term effects, where long-term may be 6000 - 8000 years of landfill leaching.

There are many laboratory leaching tests that have been reported in the literature. ASTM has developed standard leaching tests which use alternate leaching fluids with very little additional difference in the test methodology. EPA has one regulatory test for the classification of solid wastes under RCRA; the TCLP (Method 1311). EPA also has the Synthetic Precipitation Leaching Procedure (SPLP) (Method 1312). The TCLP is expected to simulate leaching of solid wastes placed in a municipal landfill, while the SPLP is designed to simulate a monodisposal situation. The TCLP and SPLP have been widely used to generate leachate concentrations for all types of solids for both inorganic and organic constituents.

At this point in his presentation, Dr. Murarka deferred to David Friedman of EPA for an explanation of the origins of the composition of the leaching fluid and the liquid-solid ratio in the TCLP. Mr. Friedman explained that there was an assumption that potentially hazardous wastes would comprise at most 5% of the volume of the material deposited in municipal solid waste

(MSW) landfills. The municipal waste was assumed to degrade and produce the acidic liquid to which the waste was exposed. Thus, this 5%/95% relationship lead to the specific composition of the acetic acid solution used in the TCLP. With respect to the 20:1 ratio of extraction fluid to waste, Mr. Friedman explained that some early leaching work performed by ASTM indicated that while the volume of leaching fluid relative to the amount of waste (e.g., the L/S ratio) did play an important role in determining the concentration of many chemicals in the leachate, there was a plateau in the L/S range around 10-20. Because there was concern with the assumption that the waste provides an infinite source of contaminants over time, using a higher L/S of 20 was seen as one way in which the TCLP could address this concern. However, as Mr. Friedman pointed out, the fact that the L/S ratio could also be expressed as "5%" was serendipitous and unrelated to the assumption that 5% of the volume of a MSW landfill was hazardous waste.

Dr. Murarka thanked Mr. Friedman for his input and pointed out that these assumptions were some of the reasons that he felt that the present consideration of leaching tests must determine if other L/S ratios may be more appropriate for other wastes or waste disposal scenarios.

Dr. Murarka stressed that he has no disagreement with the use of the TCLP in its original regulatory context, e.g., for waste classification. His concern is that there are many instances when the TCLP is used outside of that context and that many users are not familiar with the resulting limitations in the data. Over the last ten years or so, issues have arisen because of the much broader use of the TCLP and SPLP test methods. He noted that the leaching potential of a given constituent can be quite different, depending on a number of factors, such as the characteristics of the leaching fluid, the form of the chemical in the solids, and the disposal conditions. The factors that affect the leaching potential of inorganic constituents are:

- pH the pH of municipal solid waste (MSW) landfill leachate is usually in the range of 4.8 to 5.2, however, leachate from monofill or stabilized wastes is not.
- Redox conditions
- Liquid-to-solid ratio
- Solubility

Different factors affect the leaching potential of organic constituents. They are:

- Partitioning or Solubility since organic compounds are rarely available in the landfill as crystalline solids, partitioning is the predominant consideration
- Presence of organic carbon this factor will impact the concentration of the organic constituents in the aqueous phase
- Liquid-to-solid ratio
- Non-aqueous phase extraction

Dr. Murarka presented graphs depicting the concentration of constituents in the leachate vs. the pH of the leachate. He presented data for several metals, including selenium and arsenic, as well as organics such as PAHs from coal tar. The data for metals show that the overall final pH of the leachate is much more important than the pH of the actual leaching fluid itself in determining the

actual metal concentration in the leachate. Thus, which leaching fluid you start with is not as important as knowing the pH of the final leachate, and attempts to predict leachate concentrations should rely on the pH of the leachate, not the original leaching fluid.

At the end of his presentation, Dr. Murarka addressed questions from the audience. Hans van der Sloot, Netherlands Energy Research Foundation (NERF), provided extensive comments on Dr. Murarka's presentation. He began by pointing out that new landfill construction methods are in common use now, thus the original assumptions in the TCLP method may no longer be applicable. Dr. Murarka replied that this was one of the factor that he felt needed to be considered when applying leaching tests to situations other than waste classification.

Dr. van der Sloot continued, noting that based on field data, the pH versus concentration data presented by Dr. Murarka fit those data very well, and that pH could be used as a good predictor of metal concentrations in many cases. He noted that the focus on organic content should be placed exclusively on the degradable organic matter. He noted that new European Union regulations have been proposed that will ban placing any degradable organic materials at all in MSW landfills, since the breakdown of these materials lead to the acidic conditions that the TCLP was designed to model, thus keeping them out of the landfills reduces the production of organic acids, etc. Despite his agreement with much of Dr. Murarka's metals versus pH data, Dr. van der Sloot urged Dr. Murarka to be careful in applying the metals data. Dr. Murarka acknowledged that the metals situation was not as simple as it might appear, but noted that he did not have two hours in which to present a detailed discussion of metals speciation, but that he had, in fact, considered the data carefully.

One participant remarked that he had reviewed about two-thirds of the leachate data submitted under the lead paint rule and while there were some pH values as low as 4.8, most were in the range of 6.8 to 7.2, with a small group in the range of 8 to 10. These data came from both old and new landfills, with no clear pH trends apparent thus far, and that some were from MSW landfills while others were from construction debris landfills. Dr. Murarka thanked him for the information and agreed that such data would be useful in his work.

Richard Lesser, of RMRS, noted that regardless of whether EPA determines that either a single test is to be used, or multiple tests are developed for different scenarios, he felt it would be important to develop a rapid approval process for alternative tests, under the performance-based measurement system (PBMS). Otherwise, he felt it would take 8 to 9 years to get a new test considered.